

Japanese Patent Application Kokai No. 4-198303

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Polymerization Initiator and Process for Polymerization
Using the Same

Claims:

1. A radical polymerization initiator of a general formula (1):



wherein

R¹ represents an optionally substituted aliphatic hydrocarbon, an optionally substituted alicyclic hydrocarbon, or an optionally substituted aromatic hydrocarbon group; and

R², R³, and R⁴ each represents an optionally substituted aromatic hydrocarbon group.

2. A radical polymerization initiator of a general formula (2):



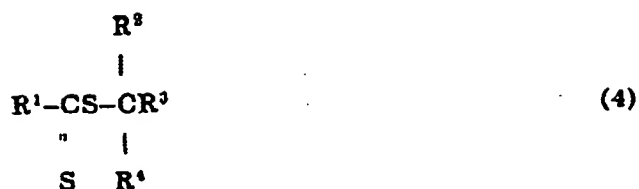
wherein R¹, R², R³ and R⁴ each has the same meaning as in Claim 1.

3. A radical polymerization initiator of a general formula (3):



wherein R¹, R², R³ and R⁴ each has the same meaning as in Claim 1.

4. A radical polymerization initiator of a general formula (4):

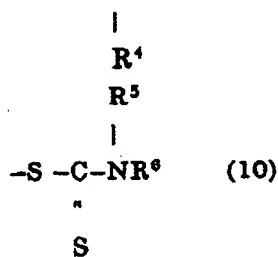
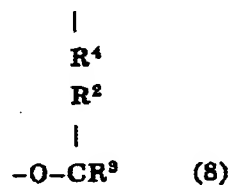
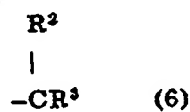
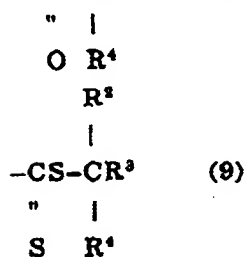
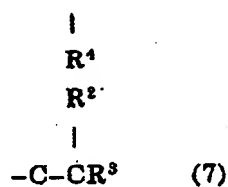
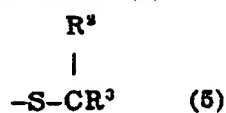


wherein R^1 , R^2 , R^3 and R^4 each has the same meaning as in Claim 1.

5. The polymerization initiator according to any one of Claims 1 - 4, wherein R^2 , R^3 and R^4 each represents an optionally substituted phenyl or naphthyl group.

6. The polymerization initiator according to any one of Claims 1 - 5, wherein R^1 is an aliphatic, alicyclic or aromatic hydrocarbon group, substituted by one or more substituents selected from a group consisting of carboxyl, sulfonyl, sulfonium, anhydrous carboxyl, formyl, cyano, isocyanato, hydroxyl, amino, ketimino, nitro, halogeno, glycidyl, triphenyl-methoxy and triphenyl-methylmercapto groups.

7. The polymerization initiator according to any one of Claims 1 - 6, wherein R^1 is an aliphatic, alicyclic or aromatic hydrocarbon group, substituted by one or more substituents among one or more of the groups of general formulae (5) - (10):



wherein

R^1 , R^2 and R^4 each has the same meaning as in Claim 1; and

R^5 and R^6 each represents an optionally substituted aliphatic hydrocarbon, an optionally substituted alicyclic hydrocarbon, or an optionally substituted aromatic hydrocarbon group.

8. The polymerization initiator according to any one of Claims 1 - 6, wherein R^1 is a group of a general formula (6):



wherein R^2 , R^3 and R^4 each has the same meaning as in Claim 1.

9. The polymerization initiator according to any one of Claims 1 - 8, wherein R^2 , R^3 and R^4 each represents a phenyl or naphthyl group substituted by one or more substituents selected from a group consisting of nitro, sulfonyl, sulfonium, cyano, carboxyl, carboxynium and halogeno groups.

10. A process for polymerizing vinyl monomers characterized in that polymerization is carried out using a polymerization initiator according to any one of Claims 1 - 9.

11. A macromolecular radical polymerization initiator characterized in comprising a polymer having at either ends and/or in side chains thereof one or more groups of a general formula (7):



wherein R^2 , R^3 and R^4 each has the same meaning as in Claim 1.

12. A macromolecular radical polymerization initiator characterized in comprising a polymer having at either ends and/or in side chains thereof one or more groups of a general formula (8):



wherein R^2 , R^3 and R^4 each has the same meaning as in Claim 1.

13. A macromolecular radical polymerization initiator characterized in comprising a polymer having at either ends and/or in side chains thereof one or more groups of a general formula (9):



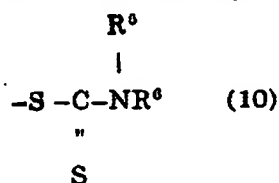
wherein R^2 , R^3 and R^4 each has the same meaning as in Claim 1.

14. The polymerization initiator according to any one of Claims 11 - 18, wherein said polymer is one or more of polymers selected from a group consisting of those of polyolefin, poly(alkylene oxide), polyester, polyamide and polyurethane types.

15. The polymerization initiator according to any one of Claims 11 - 14, wherein R^2 , R^3 and R^4 each represents an optionally substituted phenyl or naphthyl group.

16. The polymerization initiator according to any one of Claims 11 - 15, wherein R^2 , R^3 and R^4 each represents an phenyl or naphthyl group, substituted by one or more of groups selected from a group consisting of nitro, sulfonyl, sulfonium, cyano, carboxyl, carboxynium and halogeno groups.

17. A macromolecular radical polymerization initiator characterized in comprising a polymer having at either ends and/or in side chains thereof one or more groups of a general formula (10):



wherein R^5 and R^6 each represents an optionally substituted aliphatic hydrocarbon, an optionally substituted alicyclic hydrocarbon, or an optionally substituted aromatic hydrocarbon group.

18. The polymerization initiator according to 17, wherein said polymer is one or more of polymers selected from a group consisting of those of polyolefin, poly(alkylene oxide), polyester, polyamide and polyurethane types.

19. The polymerization initiator according to Claims 17 or 18, wherein R^5 and R^6 each represents a hydrocarbon group containing 1 - 10 carbon atoms.

20. A process for preparing a polymeric composition comprising polymers of block and/or graft type, characterized in reacting a polymerization initiator according to any one of Claims 11 - 19 with a vinyl monomer.

Detailed Description of the Invention

[Field of the Invention]

The present invention relates to a living radical polymerization initiator, a process for living radical polymerization using the same, and a polymeric composition comprising polymers of block and/or graft type obtainable by such a polymerization.

[Description of the Prior Art]

Several reports have been presented regarding polymerization initiators capable of initiating living radical polymerization; see for phenylazotriphenylmethane, Ootsu *et al.*, Polymer Bulletin, 16: 227 - 284 (1986); and for tetraethylthiuram disulfide, etc., Ootsu *et al.*, Polymer Bulletin, 7: 45 - 50 (1982). In either reports, it is mentioned that block copolymers of alkyl methacrylate and styrene have been synthesized using respective initiators.

[Problems to Be Solved by the Invention]

In the case of living radical polymerization using any of the above initiators, problems have arisen as follows: (1) processes to obtain polymers having higher molecular weights tend to result in wider molecular weight distributions; (2) functional groups which can be introduced at either ends of the polymers are limited to only phenyl, triphenylmethyl and diethyldithiocarbamyl groups, providing a limited number of choice for functional macromolecules; (3) higher rates of polymerization are not attainable; (4) graft matters are not obtainable; and (5) block copolymers other than those between vinyl monomers are not obtainable.

[Means to Solve the Problems]

The present inventors have made an intensive study on polymerization initiators free from the above problems and capable of initiating living radical polymerization, and processes for living radical polymerization of vinyl monomers using such initiators, resulting in the present invention, which is constituted by the following factors [1] - [4]:

[1] a radical polymerization initiator of a general formula (1):



general formula (2):



a general formula (3):



or a general formula (4):



wherein

R^1 represents an optionally substituted aliphatic hydrocarbon, an optionally substituted alicyclic hydrocarbon, or an optionally substituted aromatic hydrocarbon group;

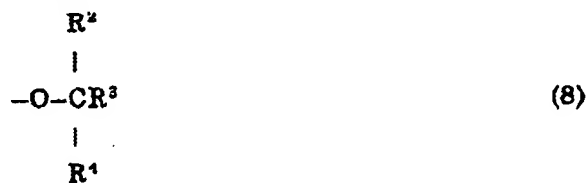
R^2 , R^3 , and R^4 each represents an optionally substituted aromatic hydrocarbon group;

[2] a process for polymerizing vinyl monomers which is carried out using a radical polymerization initiator described in [1];

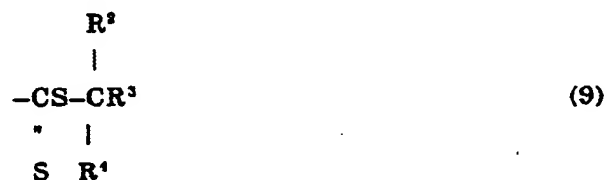
[3] a macromolecular radical polymerization initiator characterized in comprising a polymer having at either ends and/or in side chains thereof one or more groups of a general formula (7):



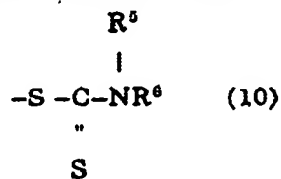
a general formula (8):



a general formula (9):



or a general formula (10):



wherein

R^2 , R^3 and R^4 each has the same meaning as above, and

12
12

R⁵ and R⁶ each represents an optionally substituted aliphatic hydrocarbon, an optionally substituted alicyclic hydrocarbon, or an optionally substituted aromatic hydrocarbon group; and

[4] a process for preparing a polymeric composition comprising polymers of block and/or graft type, characterized in reacting the macromolecular radical polymerization initiator as described in [3] with a vinyl monomer.

The group R¹ in the general formula (1) to be used in the present invention includes those listed in the following classes from (i) to (vi):

(i) saturated or unsaturated (C₁ - C₃₀)aliphatic hydrocarbon groups, such as methyl, ethyl, isopropyl, decyl, 2-ethylhexyl, stearyl, isopropenyl, 1-isobutenyl, 1-dodecyl, 2-ethylhex-2-yl groups, etc.;

(ii) saturated or unsaturated (C₃ - C₃₀)alicyclic hydrocarbon groups, such as cyclopropyl, cyclohexyl, norbornyl, ethylidene-norbornyl, 2-cyclohexylethyl, 3-cyclohexenyl groups, etc.;

(iii) saturated or unsaturated (C₆ - C₃₀)aromatic hydrocarbon groups, such as phenyl, 4-ethylphenyl, 2,4-dimethylphenyl, naphthyl, benzyl, 4-methylbenzyl, naphthylmethyl, 3-phenylpropyl, diphenylmethyl, 2,2-diphenylpropyl, triphenylmethyl, triphenylmethylethyl, tri(4-methylphenyl)methyl, diphenyl(4-methylphenyl)methylpropyl groups, etc.; and

(iv) substituted aliphatic hydrocarbon groups, such as carboxymethyl, 1,2-dicarboxyethyl, sodium carboxymethyl, 1,2-di(sodium carboxy)ethyl, 2-peroxycarboxy-2-methylethyl, dithiocarboxyethyl, 1-thiocarboxy-2-carboxyethyl, 2-sulfonylethyl, 2-sodium sulfonium ethyl, anhydrous 1,2-dicarboxyethyl, methoxycarbonylethyl, 1-ethoxycarbonyl-2-carboxyl, formylethyl, chloroformylmethyl, carbamoylmethyl, N,N-dimethyl-carbamoylmethyl, N,N-diethyl-dithiocarbamoyl, cyanoethyl, 1,2-dicyanoethyl, 6-isocyanohexyl, cyanatomethyl, 6-isocyanatoethyl, thiocyanatoethyl, thioisocyanatoethyl, formylpropyl, 2-thioformylethyl, ethylcarbonylethyl, ethylthiocarbonylethyl, 2-hydroxyethyl, 2,3-dihydroxypropyl, mercaptomethyl, hydroperoxybutyl, aminoethyl, dimethylaminoethyl, maleyliminoethyl, 3-(2-propenamino)propyl, nitropropyl, methoxyethyl, glycidyl, 2,3-diglycidylpropyl, acetylacetoxy, ethylmercapto-ethyl, bromopropyl, isopropyl-diazopropyl, propyl-hydrazinoethyl, phenoxyethyl, phenyl-mercaptomethyl, carboxyphenyl-propyl, diphenylmethoxymethyl, phenoxyethyl, 3-(triphenylmethoxy)-propyl, triphenylaminopropyl, diphenylmethyl-mercaptoethyl, triphenyl-methylmercaptoethyl, 2-phenoxy-carbonylethyl, tri(4-nitrophenyl)methyl-mercaptoethyl, tri(4-sulfonylphenyl)methyl-mercaptoethyl, tri(4-sodium sulfonium phenyl)methyl-mercaptoethyl, 2,3-bis(triphenylmethyl-mercapto)propyl, 2-nitro-3-(triphenyl-methylmercapto)propyl, 3,6,9-tris(triphenyl-ethylmercato)decyl, 5-triphenylmethylmercapto-8-triphenyl-

ethylmercaptomethylpentyl, 2,3,4-tris[tri (4'-nitrophenyl)methyl-mercapto]butyl groups, etc.;

(v) substituted alicyclic hydrocarbon groups, such as carboxycyclohexyl, isocyanocyclohexylmethyl, 2,5-diisocyanatocyclohexyl, methoxycyclohexylpropyl, 4-triphenylmethylcyclohexyl, 2,5-oxacyclohexyl, 2-methoxynorbornyl, tri(4-nitrophenyl)methyl-mercaptocyclohexyl groups, etc.; and

(vi) substituted aromatic hydrocarbon groups, such as 4-triphenylmethylmercaptophenyl, diphenylnaphthyl-methylmercaptoethyl-benzyl, 4-carboxyphenyl, tri(4-carboxyphenyl)methyl, tri(4-sodium carboxynium phenyl)methyl, 4-peroxycarboxybenzyl, dithiocarboxyphenyl, 4-sulfonylbenzyl, tri(4-sulfonylphenyl)methyl, 4-sodium sulfonium phenyl, tri(4-sodium sulfonium phenyl)methyl, methoxycarbonylphenyl, 2-phenyloxycarbonylmethylphenyl, 4-formylphenyl, chloroformylbenzyl, carbamoylphenyl, 4-cyanophenyl, 2,4-dicyanophenyl, diphenyl(4-cyanophenyl)methyl, tri(4-cyanophenyl)methyl, 4-isocyanobenzyl, cyanatophenyl, 4-isocyanato-3-methylphenyl, thiocyanatophenyl, thioisocyanatophenyl, ethylcarbonylphenyl, ethylthiocarbonylbenzyl, 4-glycidyl-phenylethyl, 2-hydroxyphenyl, 3-hydroxynaphthyl, mercaptophenyl, hydroperoxybenzyl, aminophenyl, dimethylamino-ethylbenzyl, 4-nitrophenyl, 3-methoxyphenyl, 4-di(4-nitrophenyl)phenylmethyl-mercaptoethylphenyl, tri(4-nitrophenyl)methyl, 3,5-dimethoxyphenyl, phenoxyphenyl, phenoxymethyl, ethylmercapto-phenyl, phenylmercaptobenzyl, bromophenyl, triphenylmethyl-mercaptoethylbenzyl, 2,4-dichlorobenzyl, tri(4-bromophenyl)methyl, tri(4-chlorophenyl)methylmercaptohexyl, isopropyl-diazomethylphenyl, triphenylmethylmercaptophenyl, bis(triphenylmethyl-mercapto)phenyl groups, etc.

Among the groups illustrated in (i) - (vi), preferred groups as R' are those from the following (A) - (C):

(A) the groups, among those in (iv) - (vi), having one or more substituents among one or more of the groups selected from carboxyl, sulfonyl, sulfonium, anhydrous carboxyl, dithiocarbamoyl, cyano, isocyanato, hydroxyl, amino, nitro, halogeno, glycidyl, phenyl, naphthyl, triphenylmethoxy and triphenylmethylmercapto groups;

(B) the groups, among those in (iv) - (vi), substituted by one or more substituents among one or more of groups of general formula (7):



a general formula (8):



a general formula (9):



or a general formula (10):



wherein $R^2 - R^6$ each has the same meaning as above, with those in which each of R^2 , R^3 and R^4 is either phenyl or naphthyl groups substituted by one or more substituents among one or more groups selected from phenyl, naphthyl, nitrophenyl, nitronaphthyl, sulfonyl, sulfonium, cyano, carboxyl, carboxynium and halogeno groups being particularly preferred; and

(C) the groups, among those in (iii) or (vi), being optionally substituted aromatic hydrocarbon groups of general formula (6):



wherein R^2 , R^3 and R^4 each has the same meaning as above, with those in which each of R^2 , R^3 and R^4 is either phenyl or naphthyl groups substituted by one or more substituents among one or more groups selected from phenyl, naphthyl, nitrophenyl, nitronaphthyl, sulfonyl, sulfonium, cyano, carboxyl, carboxynium and halogeno groups being particularly preferred.

All or one of the optionally substituted aromatic hydrocarbon groups of R^2 , R^3 and R^4 in general formulae (1) - (9) may be different from others.

Examples of the optionally substituted aromatic hydrocarbon groups of R^2 , R^3 and R^4 are those from the following (a) - (d):

(a) unsubstituted aromatic hydrocarbon groups, such as phenyl, naphthyl, anthranil, benzyl, 1-phenylethyl, 4-phenylbutyl groups, etc.;

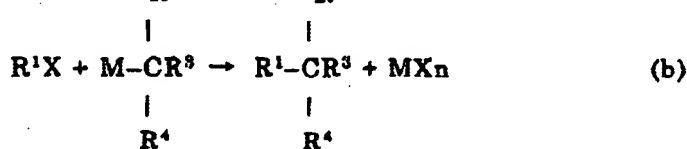
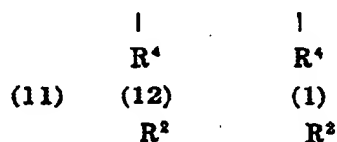
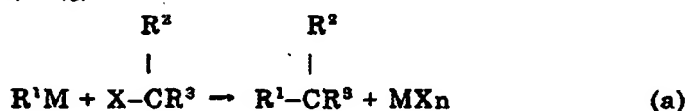
(b) substituted phenyl groups, such as 4-methylphenyl, 3-isopropylphenyl, 4-phenylphenyl, 4-carboxyphenyl, dithiocarboxyphenyl, 4-sulfonylphenyl, 4-sodium sulfonium phenyl, methyloxy-carbonylphenyl, 2-phenyloxy-carboxymethylphenyl, carbamoylphenyl, 4-cyanophenyl, 1,4-dicyanophenyl, cyanatophenyl, 4-isocyanato-3-methylphenyl, thiocyanatophenyl, thioisocyanatophenyl, 2-thioformyl-ethylphenyl, ethylcarbonylphenyl, 2-hydroxyphenyl, mercaptophenyl, aminophenyl, 4-nitrophenyl, 3-methoxyphenyl, 3,5-dimethoxyphenyl, phenoxyphenyl, ethylmercaptophenyl, bromophenyl, isopropyl-diazomethylphenyl groups, etc.;

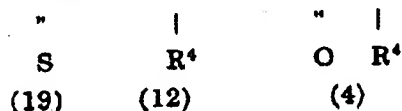
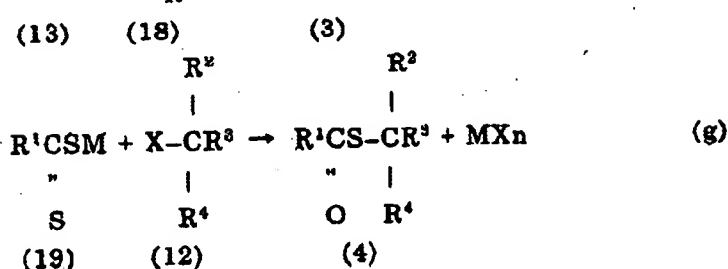
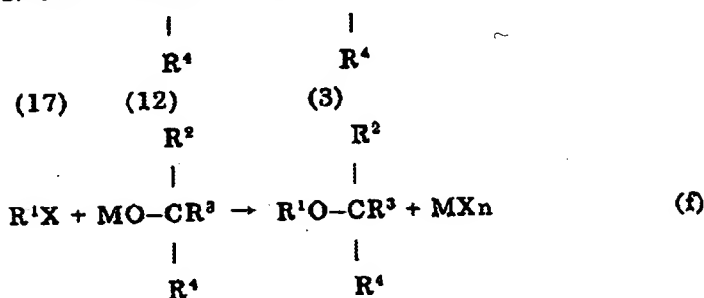
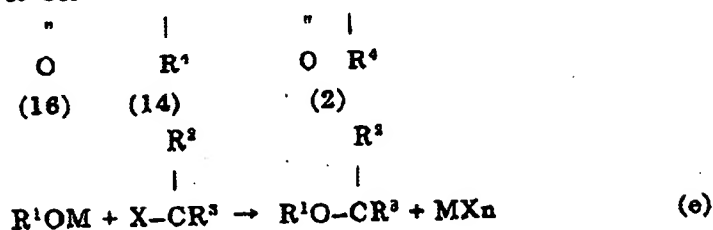
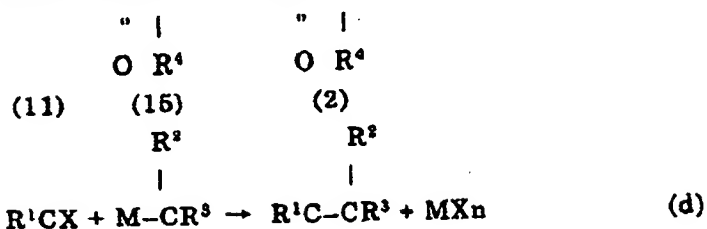
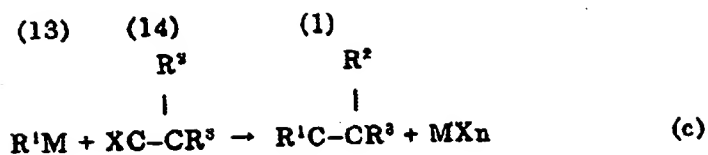
(c) substituted naphthyl groups, such as 3-methyl-1-naphthyl, 6-carboxy-2-naphthyl, 5,8-disulfonyl-1-naphthyl, 6-nitro-1-naphthyl groups, etc.; and

(d) other aromatic hydrocarbon groups, such as carboxybenzyl, dithiocarboxy-phenylethyl, 4-sulfonylbenzyl, 4-sodium sulfonium benzyl, 2-phenyloxy-carbonylethyl, chloroformylbenzyl, 4-cyanobenzyl, 4-formyl-2-ethylbenzyl, ethylcarbonylbenzyl, ethylthiocarbonylbenzyl, hydroperoxybenzyl, dimethylamino-ethylbenzyl, 4-nitrobenzyl, phenoxybenzyl, phenoxymethyl, phenylmercaptomethyl, phenylmercaptobenzyl, 2,4-dichlorobenzyl groups, etc.

Among these groups, preferred groups are phenyl and naphthyl groups, substituted phenyl groups of (b), and substituted naphthyl groups of (c), with phenyl and naphthyl groups both unsubstituted or substituted by one or more substituents among one or more of the groups selected from nitro, sulfonyl, sulfonium, cyano, carboxyl, carboxynium and halogeno groups being particularly preferred.

Examples of typical processes for preparing radical polymerization initiators [1] include the processes described in the following reaction formulae (a) - (g):





wherein

R^1 . R^4 each has the same meaning as above,

X represents a halogen atom,

M represents a metal selected from Li, Mg, Cd, Na, K, Al, etc., and

n is an integer from 1 to 3.

In processes (a) and (b), the inventive polymerization initiator [1] having the general formula (1) can be obtained by carrying out dehalogenative metalation reactions of (11) with (12), and of (13) with (14), respectively.

In processes (c) and (d), another type of the inventive polymerization initiator [1] having the general formula (2) can be obtained by carrying

out dehalogenative metalation reactions of (11) with (15), and of (16) with (14), respectively.

In processes (e) and (f), further type of the inventive polymerization initiator [1] having the general formula (3) can be obtained by carrying out dehalogenative metalation reaction of (17) with (12), and of (13) with (18), respectively.

In process (f), still another type of the inventive polymerization initiator [1] having the general formula (4) can be obtained by carrying out a dehalogenative metalation reaction of (19) with (12).

Respective dehalogenation metalation reactions are usually performed in basic solvents, or in appropriate organic solvents in the presence of a basic catalyst. Examples of the basic solvents include pyridine, methylpyridine, triethylamine, dimethylformamide and the like. Examples of the basic catalysts include dimethylpyridine, dimethylaminopyridine, DBU, DBN, sodium hydroxide, potassium hydroxide, sodium methoxide and the like. Examples of the appropriate organic solvents include benzene, toluene, xylene, ethanol, dimethylsulfoxide, tetrahydrofuran, dioxane, acetone, methyl ethyl ketone, cyclohexanone, heptane, kerosine, dimethylformamide and the like.

Reaction conditions for the above processes (a) and (b) are not specifically limited, and vary depending on the type of raw materials, the type of solvents to be used and others. For example, the polymerization temperature usually ranges from -80 to 250°C, preferably from 0 to 120°C, and the reaction pressure is between 1 and 3 atm, and preferably at 1 atm. The reaction time usually ranges from 0.5 to 36 hours, preferably from 1 to 24 hours. The concentration for the reaction usually ranges from 1 to 90%, preferably from 10 to 60%.

The macromolecular radical polymerization initiator [3] can be derived from various polymers. As the polymer, (i) polyolefinic polymers, (ii) polyvinyl polymers, (iii) olefin-vinyl copolymers, (iv) poly(alkylene oxide)-type polymers, (v) polyester polymers, (vi) polyamidic polymers, (vii) polyimidic polymers, (viii) polyurethane polymers, and (ix) polyureic polymers can be illustrated.

(i) polyolefinic polymers include single, binary and multicomponent polymers of olefinic monomers, and modification thereof. Examples of olefinic monomer are: ethylene; ($C_1 - C_{30}$)olefins, such as propylene, butene, 4-methylpentene-1, heptene, nonene, isodecene and eicosene; alicyclic olefins, such as cyclopentene, cyclohexene, 3-methylcycloheptene, cyclooctene, norbornene and 2-ethylnorbornene; dienes, such as butadiene, isoprene, cyclopentadiene and ethylidene-norbornene; and the like.

(ii) polyvinyl polymers include single, binary and multicomponent polymers of vinyl monomers, and modification thereof. Examples of

vinyl monomer are: styrene; substituted styrenes, such as sodium p-styrenesulfonate, α -methylstyrene and p-ethylstyrene; (meth)acryloyl-containing monomers, such as (meth)acrylonitrile, (meth)acrylamide, (meth)acrylic acid, sodium (meth)acrylate, esters of (meth)acrylic acid with ($C_1 - C_{30}$)alcohols, amides of (meth)acrylic acid with ($C_1 - C_{30}$)amines, hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate, N,N-dimethyl-aminoethyl (meth)acrylate, adducts of (meth)acrylic acid and hydroxyethyl (meth)acrylate with 1 - 100M of alkylene oxides (ethylene oxide and/or propylene oxide and/or styrene oxide); N-vinylpyrrolidone; maleic monomers, such as maleic anhydride, half- and di-esters of maleic anhydride with ($C_1 - C_{30}$)alcohols, and mono- and di-amides and imides of maleic anhydride with ($C_1 - C_{30}$)amines; vinyl chloride; vinyl acetate; allyl alcohol; adducts of allyl alcohol with 1- 100M of alkylene oxide; divinylbenzene; vinyl (meth)acrylate; and the like.

(iii) olefin-vinyl copolymers include copolymers of the olefinic monomers illustrated in (i), vinyl monomers illustrated in (ii), and the like.

(iv) poly(alkylene oxide)-type polymers include single, binary and multicomponent polymers of alkylene oxides, and modification thereof. Examples of alkylene oxide are: ethylene oxide; propylene oxide; styrene oxide; glycidyl (meth)acrylate; epichlorohydrin; glycidol; glycidyl ethers, such as butyl glycidyl ether, phenyl glycidyl ether, mono- and di-glycidyl ether of poly(ethylene glycol); poly(tetramethylene oxide); and the like.

(v) polyesteric polymers include polyesters of polybasic acids with polyhydric alcohols, those polyesters with caprolactone, etc., and modification thereof. Examples of polybasic acid are divalent acids, such as oxalic, succinic, adipic, pimelic, sebacic, 4-propyl-2-pentenoic, malonic, maleic, maleic anhydride, fumaric, phthalic, phthalic anhydride, terephthalic, naphthalenedicarboxylic, and quinolinediacetic; and/or acids having 3 or more valencies, such as glycerol, 1,2,3-butanetricarboxylic acid and butane-1,2,3,4-tetracarboxylic acid. Examples of polyhydric alcohol are dihydric alcohol, such as ethylene glycol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 1,8-octanediol, hydroquinone, bisphenol A, and alkylene oxide adducts thereof, polybutadienediol, hydrogenated polybutadienediol, polyisoprenediol and polystyrenediol; and/or alcohols having three or more valencies, such as glycerol, polyglycidol, pentaerythritol, and alkylene oxide adducts thereof; and the like. Examples of caprolactone are 7-caprolactone, ϵ -caprolactone and others.

(vi) polyamidic polymers include polyamides of polybasic acids as described in (v) with multivalent amines, those polyamides with caprolactum, etc., and modification thereof. Examples of multivalent amines are ethylenediamine, triethylenetetramine, 1,4-diamino-

cyclohexane, 1,4-diaminobenzene, 1,4-diaminomethylbenzene and the like. Examples of caprolactum are 7-caprolactum, 8-caprolactum and others.

(vii) polyimidic polymers includes polyimides of multivalent amines as described in (vi) with compounds having two or more acid anhydride groups within a molecule, such as pyromellitic anhydride etc., and modification thereof.

(viii) polyurethanic polymers include polyurethanes of polyhydric alcohols as described in (v) and/or poly(alkylene oxide)-type polymers as in (iv) and/or polyesteric polymers as in (v) with multivalent isocyanates, etc., and modification thereof. Examples of multivalent isocyanate are 2,6-tolylene-diisocyanate, 4,4'-diphenylmethane-diisocyanate, 1,4-cyclohexane-diisocyanate, 1,8-hexane-diisocyanate, 1,3,5-benzene-triisocyanate and others.

(ix) polyureic polymers include polyureas of multivalent amines as mentioned in (vi) with multivalent isocyanates as mentioned in (viii), and the like.

These polymers can be modified or altered with various functional groups. Preferred polymers among these are polyolefinic polymers (i), poly(alkylene oxide)-type polymers (iv), polyesteric polymers (v), polyamidic polymers (vi), and polyurethanic polymers (viii).

The weight average molecular weight of these polymers usually ranges from 500 to 1,000,000, though varies depending on the type of polymers.

As typical processes for synthesizing the macromolecular radical polymerization initiator [3], there can be mentioned those described in the following (A) - (H). In each formula, $R^1 - R^4$ each has the same meaning as above, X represents halogen atoms, M represents metals such as Li, Mg, Cd, Na, K, Al, etc..

(A) a process wherein a radical $-COOH$ in a polymer having carboxylic acid groups at either ends and/or in the side chains thereof is converted to a radical $-COX$, and thereafter reacted with a compound of general formula (14):



wherein R^2 , R^3 and R^4 each has the same meaning as above.

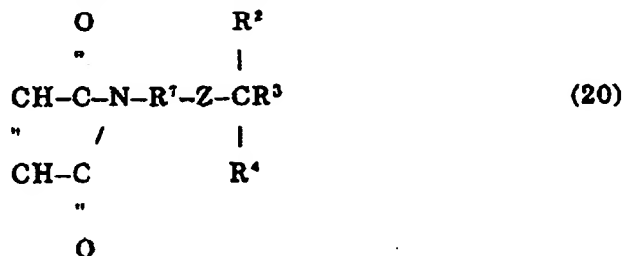
The polymer having carboxylic acid groups at either ends and/or in the side chains thereof includes, for example, among the above polymers, reaction products of poly(alkylene oxide)-type polymers (iv), polyesteric polymers (v) or polyurethanic polymers (viii) with polybasic acids; copolymers, among polyvinyllic polymers (ii), of vinyllic monomers

process wherein alkylene oxide or others is added to copolymers of carboxylic acid-containing monomers among polyvinyllic polymers (ii), such as (meth)acrylic acid, maleic acid and others; a process wherein graft addition of hydroxyl group-containing monomers among vinyllic monomers to polyolefinic polymers (i) is carried out; and other processes.

Process to convert hydroxyl group to a radical -OM using known methods includes, for example, a process to react with metal sodium, metal lithium or metal potassium, and other processes.

Process (B) yields the macromolecular radical polymerization initiator [3] having a group of general formula (8).

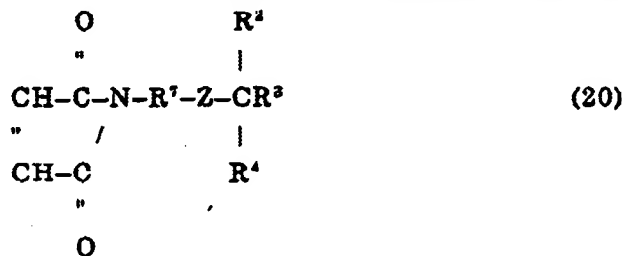
(C) a process wherein a compound of general formula (20):



wherein R^2 , R^3 and R^4 each has the same meaning as above, and R^1 represents an aliphatic or aromatic hydrocarbon group, and Z represents any one of O, C=O or CSS, is thermally added to double bonds of a double bond-containing polymer.

Examples of double bond-containing polymers include polybutadiene, polyisoprene, and copolymers of olefinic monomer and dienes among polyolefinic polymers (i); thermal degradation products of polyolefinic polymers (i); those synthesized with polybasic acid having unsaturated double bonds, such as 4-propyl-2-pentenoic, maleic, fumaric and other acids, among polyesteric polymers (v), polyamidic polymers (vi) and polyurethanic polymers; and the like.

(D) a process wherein a compound of general formula (20):



wherein R^2 , R^3 , R^4 , R^1 and Z each has the same meaning as above, is subjected to a radical addition to any of the polymers from (i) to (ix) in the presence of a peroxide catalyst.

As the peroxide catalyst, there are mentioned benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, etc.. The amount of the peroxide catalyst to

be used usually ranges from 0.01 to 5%, preferably from 0.1 to 3% based on the weight of the compound of general formula (20).

Processes (C) and (D) yield the macromolecular radical polymerization initiator [3] having a group of any of general formulae (7) - (9).

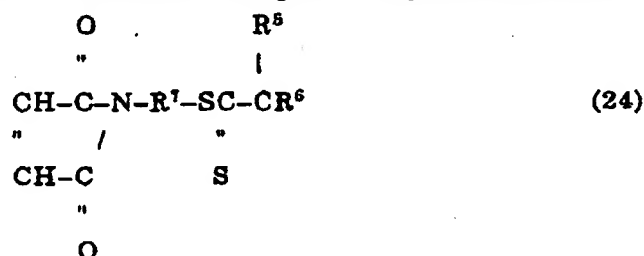
(E) a process wherein hydroxyl group of a polymer having hydroxyl groups at either ends and/or in the side chains thereof is converted to a radical -X, and thereafter reacted with a compound of general formula (23):



wherein R^5 and R^6 each has the same meaning as above.

The polymer having hydroxyl groups at either ends and/or in the side chains thereof includes those illustrated in (B) above. The process to convert hydroxyl group to radical -X includes a process to react with hydrogen halides.

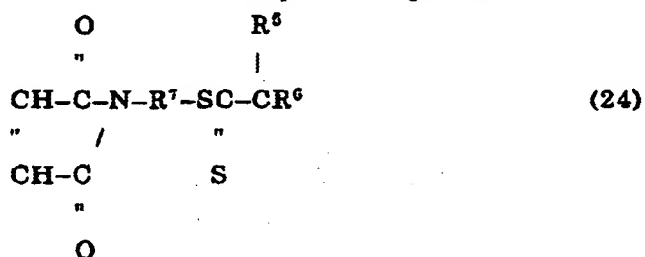
(F) a process wherein a compound of general formula (24):



wherein R^5 , R^6 and R^7 each has the same meaning as above, is thermally added to double bonds of a double bond-containing polymer.

Examples of double bond-containing polymers include those mentioned in (C) above.

(G) a process wherein a compound of general formula (24):



wherein R^5 , R^6 and R^7 each has the same meaning as above, is subjected to a radical addition to any of the polymers from (i) to (ix) in the presence of a peroxide catalyst.

As the peroxide catalyst, there are mentioned benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, etc. The amount of the peroxide catalyst to

containing carboxylic acid groups, such as half-esters of (meth)acrylic acid or maleic anhydride with ($C_1 - C_{30}$)alcohols, etc.; polymers wherein vinyl monomers capable of living anion polymerization, such as styrene, methyl (meth)acrylate, butyl (meth)acrylate, acrylonitrile, butadiene, isoprene, etc., are polymerized using living anion polymerization, and thereafter reacted with carbon dioxide to introduce carboxylic acid groups to either ends thereof; and polymers wherein carboxylic acid groups have been introduced therein by a variety of modifications. As the process to introduce carboxylic acid groups into the polymers by modification, there can be mentioned a process wherein maleic anhydride copolymer among polyvinyl polymers (ii) is hydrolyzed; a process wherein graft addition of monomers, among vinylic monomers, containing carboxylic acid groups to polyolefinic polymers (i) is carried out; and other processes.

Process to convert a radical $-COOH$ to $-COX$ includes, for example, a process to react with thionyl halide or phosphorus halide, and others.

Process (A) yields the macromolecular radical polymerization initiator [3] having a group of general formula (7).

(B) a process wherein hydroxyl group of a polymer having hydroxyl groups at either ends and/or in the side chains thereof is converted to a radical $-OM$ using a known method, and thereafter reacted with a compound of general formula (12):



wherein R^1 , R^2 and R^4 each has the same meaning as above.

The polymer having hydroxyl groups at either ends and/or in the side chains thereof includes, for example, among the above-mentioned polymers, poly(alkylene oxide)-type polymers (iv); polyester polymers (v); polyurethane polymers (viii); copolymers of vinylic monomers containing hydroxyl group, among polyvinyl polymers (ii), such as allyl alcohol, hydroxyethyl (meth)acrylate, etc.; polymers wherein vinyl monomers capable of living anion polymerization, such as styrene, methyl (meth)acrylate, butyl (meth)acrylate, acrylonitrile, butadiene, isoprene, etc., are polymerized using living anion polymerization, and thereafter reacted with oxygen, ethylene oxide or others to introduce hydroxyl groups to either ends thereof; and polymers wherein hydroxyl groups have been introduced therein by a variety of modifications. As the process to introduce hydroxyl group into the polymers by modification, there can be mentioned a process wherein copolymers of glycidyl (meth)acrylate, vinyl acetate or others among polyvinyl polymers (ii) are hydrolyzed; a

be used usually ranges from 0.01 to 5%, preferably from 0.1 to 3% based on the weight of the compound of general formula (20).

Processes (E) through (G) yield the macromolecular radical polymerization initiator [3] having a group of general formula (10).

The reaction condition in which these polymerization initiators [3] are synthesized by processes as shown in (A) - (G) above, has no specific limitation, and varies depending on the type of raw materials, the type and concentration of solvent to be used, etc. For example, the temperature of polymerization usually ranges from -80 to 250°C, and preferably from 0 to 180°C, and the reaction pressure is usually between 1 and 3 atm, and preferably a value of 1 atm. The reaction time usually ranges from 0.5 to 38 hours, and preferably from 1 to 12 hours. The reaction concentration usually ranges from 1 to 90%, and preferably from 10 to 60%.

Said vinyl monomer to be used in the processes [2] and [4] according to the present invention may be any vinyl monomers capable of radical polymerization, having no specific limitation. Examples are, for example, vinylic monomers exemplified in (ii) on polymers which constitute radical polymerization initiators [3], butadiene, isoprene, and the like. These vinyl monomers may be used alone or in combination with two or more monomers.

In the processes [2] and [4] according to the present invention, the polymerization condition has no specific limitation, and varies depending on the type and amount of initiator [1] or [3] to be used, the type and amount of vinyl monomers to be used, the type of solvents to be used as required, etc.

The amount of polymerization initiator [1] or [3] to be used varies depending on the molecular weight of polymers required, and usually ranges from 0.0001 to 2,000mM, and preferably from 0.01 to 100mM per 1M of the monomer.

The polymerization temperature usually ranges from -80 to to 250°C, and preferably from 50 to 180°C. The reaction pressure usually ranges from -0.1 to 3,000atm, and preferably from 0.5 to 50atm. The reaction time usually ranges from 0.5 to 36 hours, and preferably from 1 to 12 hours.

Solvents can be used as required. The reaction may be carried out in bulk using said vinyl monomer as the solvent. When solvents are used, the concentration thereof may vary depending on the type of monomers, the molecular weight of aimed polymer, the reaction temperature, etc. This concentration usually ranges from 3 to 99%, and preferably from 30 to 99%.

The type of solvents to be used as required has no specific limitation. Examples include customary aqueous solvents, such as water, water/methanol, water/isopropyl alcohol, and other mixture systems; hydrocarbonaceous solvents, such as heptane, cyclohexane, isoparaffin, mineral oils, benzene, toluene, xylene, tetralin, etc.; chloric solvents, such as ethylene dichloride, carbon tetrachloride, chlorobenzene, chlorinated paraffins, etc.; and the like. In addition to these, there can be used alcoholic solvents, such as ethanol, isopropyl alcohol, benzyl alcohol, ethylene glycol, poly(propylene glycol), poly(tetramethylene glycol), etc.; etheric solvents, such as diethyl ether, dioxane, tetrahydrofuran, diphenyl ether, etc.; ketonic solvents, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, etc.; esteric solvents, such as ethyl acetate, dibutyl phthalate, etc.; amidic solvents, such as acetamide, dimethylacetamide, dimethylformamide, etc.; sulfoxidic solvents, such as dimethylsulfoxide, etc.; acidic solvents, such as acetic acid, trifluoroacetic acid, phenol, benzoic acid, etc.; basic solvents, such as triethylamine, pyridine, etc.; and others.

The polymerization method also has no specific limit, with polymerization in homogeneous systems, precipitation polymerization, emulsion polymerization, suspension polymerization, pearl polymerization, and the like being applicable. Obtaining homopolymers from one vinyl monomer species, random copolymers from two or more of vinyl monomer species, and block copolymers by polymerizing one vinyl monomer species, followed by polymerizing another species are also feasible. The conditions for polymerization are in general similar to those exemplified for preparing the polymerization initiators [4] above.

In the process [2] according to the present invention, a polymer composition comprising homopolymers will be obtained, when one vinyl monomer species is used, while concurrent use of two or more of vinyl monomer species will result in a polymer composition comprising random copolymers. A polymer composition comprising block polymers between vinyl monomers can be obtained by polymerizing one vinyl monomer species, followed by polymerizing another vinyl monomer species.

In the process [4] according to the present invention, a polymer composition comprising block polymers will be obtained from, among the initiators [3], those having a group of any one of general formulae (7) - (10) only at either ends of their principal chain, while those having one or more of the groups of any one of general formulae (7) - (10) in their side chains will result in graft copolymers.

Compositions resulted from, among the processes [2] according to the present invention, and those wherein one vinyl monomer species is polymerized, followed by polymerizing another vinyl monomer species, as

well as compositions resulted from the processes [4], comprise a mixture of block and/or graft matters as the polymer component, and homopolymers which have not been involved in said block and/or graft polymerization. Such homopolymers, however, can be purified off or removed. Thus, the content of block and/or graft matters in the polymer component for the present composition usually ranges from 40 to 100%, and preferably from 70 to 100%. The molecular weights of the block and/or graft matters have no specific limitation, though normally range from 500 to 2,000,000, and preferably from 100 to 500,000.

The purification process in the case of collecting the purified product of block and/or graft polymers from the present composition has no specific limitation, and includes (i) processes utilizing the difference among the solubilities in solvents, such as solvent extraction, solvent precipitation, column chromatography, etc.; and (ii) processes utilizing the difference among the molecular weights, such as preparative gel permeation, membrane dialysis, etc., and others.

The present composition may contain various solvents in addition to the polymer component. As the solvents, there are mentioned reaction solvents as described above in the processes [2] and [4] according to the present invention, and the like. The content of solvents usually ranges from 3 to 99%, and preferably from 30 to 99%.

Among the present compositions, those having a group of general formula (6), which are capable of radical polymerization, can be used as the initiator [4] according to the present invention.

The process [2] for polymerizing vinyl monomers using the initiator [1] according to the present invention, enables to obtain polymers with narrower molecular weight distributions, which have not been obtainable in the prior art processes, and to obtain with higher yields polymers having various functional groups at either ends of the principal or side chains thereof. Besides, using a polymerization initiator having three or more of the groups of general formulae (5) - (9) among the initiators [1], it is possible to obtain polymers of increased molecular weights in a short time, and to synthesize star polymers.

The process among the processes [2] according to the present invention, wherein one type of vinyl monomers is polymerized, and then another type of vinyl monomers is polymerized, as well as the process [4] wherein a vinyl monomer is polymerized using a polymerization initiator [3] according to the present invention, provide a block and/or graft polymer composition. In this case, it is possible to obtain the block and/or graft polymer with elevated yields, and to obtain a block and/or graft matter between incompatible segments. In this case, the initiators [3] having the groups of general formulae (7) - (10) at either ends of the principal chain

only will result in block polymers, while those containing one or more groups of general formulae (7) - (10) in the side chains will result in graft copolymers. Among the initiators [3], in particular, those based on the polymers other than polyvinyl polymers will result with elevated yields in non-vinyl-vinyl block and/or graft copolymers, which has not been obtainable in the prior art processes.

[Examples]

The present invention is now described in further detail in the following preparative and practical examples, which are never intended to limit the invention. As used therein, part means part by weight, and % means % by weight.

Preparative Example 1

In a nitrogen-replaced glass reactor, 30 parts of anhydrous toluene, 5.6 parts of triphenylmethyl chloride were fed, and 9 parts of a 15% solution of butyllithium in hexane was added dropwise at room temperature over a period of about 30 minutes. As addition proceeded, a white precipitation was generated. After the dropwise addition, the mixture was stirred for an hour, and filtered off the white precipitation. After washing the filtrate with water, the raw materials and by-products as well as toluene were distilled off under reduced pressure to yield 5.1 parts of butyl-triphenylmethane (BuTPM), a polymerization initiator [1] according to the present invention.

Preparative Example 2

The procedure in Preparative Example 1 was followed, except that 3.9 parts of benzylmagnesium bromide were added instead of 9 parts of a 15% solution of butyllithium in hexane, to yield 5.2 parts of benzyl-triphenylmethane (BzTPM), an initiator [1] according to the present invention.

Preparative Example 3

The procedure in Preparative Example 1 was followed, except that 21 parts of a 15% solution of dimethyl oxalate-2-sodium in hexane were added instead of 9 parts of a 15% solution of butyllithium in hexane, to yield 6.5 parts of dimethyl-2-triphenylmethyl oxalate (MTPMO), an initiator [1] according to the present invention.

Preparative Example 4

The procedure in Preparative Example 1 was followed, except that 7.5 parts of tri(4-chlorophenyl)methyl chloride were added instead of 5.6 parts of triphenylmethyl chloride, to yield 6.0 parts of butyl-tri(4-chlorophenyl)methane (BuTCPM), an initiator [1] according to the present invention.

Preparative Example 5

The procedure in Preparative Example 2 was followed, except that 8.5 parts of tri(4-nitrophenyl)methyl chloride were added instead of 5.6 parts of triphenylmethyl chloride, to yield 8.2 parts of benzyl-tri(4-nitrophenyl)methane (BzTNPM), an initiator [1] according to the present invention.

Preparative Example 6

The procedure in Preparative Example 4 was followed, except that 15.8 parts of a 15% solution of ethylen-bismagnesium bromide in ethylene dichloride were added instead of 9 parts of a 15% solution of butyllithium in hexane, to yield 6.5 parts of [tri(4-chlorophenyl)methyl]ethylene (BTCPME), an initiator [1] according to the present invention.

Preparative Example 7

In a nitrogen-replaced glass reactor, 30 parts of anhydrous toluene, 6.1 parts of triphenylacetic chloride were fed, and 14.3 parts of a 15% solution of dibutylcadmium in hexane was added dropwise over a period of about 30 minutes. As addition proceeded, a white precipitation was generated. After the dropwise addition, the mixture was stirred for an hour, and filtered off the white precipitation. After washing the filtrate with water, the raw materials and by-products as well as toluene were distilled off under reduced pressure to yield 5.9 parts of butyl triphenylmethyl ketone (BuTPMK), an initiator [1] according to the present invention.

Preparative Example 8

The procedure in Preparative Example 7 was followed, except that 2.9 parts of dibenzylcadmium were added instead of 14.3 parts of a 15% solution of dibutylcadmium in hexane, to yield 6.8 parts of benzyl triphenylmethyl ketone (BzTPMK), an initiator [1] according to the present invention.

Preparative Example 9

The procedure in Preparative Example 7 was followed, except that 2.9 parts of di(methyloxycarbonyl)ethylcadmium were added instead of 14.3 parts of a 15% solution of dibutylcadmium in hexane, to yield 6.5 parts of methyloxycarbonyl ethyl triphenylmethyl ketone (OCTPMK), an initiator [1] according to the present invention.

Preparative Example 10

The procedure in Preparative Example 7 was followed, except that 7.9 parts of tri(4-methoxyphenyl)acetic chloride were added instead of 6.1 parts of triphenylacetic chloride, to yield 6.8 parts of butyl tri(4-methoxyphenyl)methyl ketone (BTCPMK), an initiator [1] according to the present invention.

Preparative Example 11

The procedure in Preparative Example 7 was followed, except that 32.0 parts of a 30% solution of tri(4-nitrophenyl)methylmagnesium bromide in diethylene chloride were added instead of 14.3 parts of a 15% solution of dibutylcadmium in hexane, and 3.0 parts of 2-cyanoacetic bromide were added instead of 6.1 parts of triphenylacetic chloride to yield 9.9 parts of 2-cyanomethyl tri(4-nitrophenyl)methyl ketone (CENPMK) an initiator [1] according to the present invention.

Preparative Example 12

The procedure in Preparative Example 11 was followed, except that 2.6 parts of glutaric dibromide were added instead of 3.0 parts of 2-cyanoacetic bromide, to yield 9.5 parts of 1,3-bis[tri(4-nitrophenyl)-methylcarbonyl]propane (BTNPCP), an initiator [1] according to the present invention.

Preparative Example 13

In a nitrogen-replaced glass reactor, 30 parts of toluene, 5.6 parts of triphenylmethyl chloride were fed, and after stirring to a homogeneous mixture, 27.7 parts of a 15% solution of sodium dodecylate in THF was added dropwise at room temperature over a period of 15 minutes. After the dropwise addition, a white precipitation was generated. After stirring at room temperature for an hour, the white precipitation was filtered off, and pyridine and raw materials were distilled off under reduced pressure to yield 6.5 parts of dodecyl triphenylmethyl ether (DTPME), a polymerization initiator [1] according to the present invention.

Preparative Example 14

The procedure in Preparative Example 13 was followed, except that 17.3 parts of a 15% solution of sodium benzyl alcoholate in THF were added instead of 27.7 parts of a 15% solution of sodium dodecylate in THF, to yield 6.0 parts of benzyl triphenylmethyl ether (BTPME), an initiator [1] according to the present invention.

Preparative Example 15

The procedure in Preparative Example 13 was followed, except that 16.8 parts of a 15% solution of sodium methyloxycarbonyl-ethylate in THF were added instead of 27.7 parts of a 15% solution of sodium dodecylate in THF, to yield 6.3 parts of methyloxycarbonylethyl triphenylmethyl ether (OETPME), an initiator [1] according to the present invention.

Preparative Example 16

The procedure in Preparative Example 13 was followed, except that 7.5 parts of tri(4-chlorophenyl)methyl chloride were added instead of 5.6 parts of triphenylmethyl chloride, to yield 8.0 parts of dodecyl tri(4-chlorophenyl)methyl ether (DTCPME), an initiator [1] according to the present invention.

Preparative Example 17

The procedure in Preparative Example 14 was followed, except that 8.5 parts of tri(4-nitrophenyl)methyl chloride were added instead of 5.6 parts of triphenylmethyl chloride, to yield 8.2 parts of benzyl tri(4-nitrophenyl)methyl ether (BTNPME), an initiator [1] according to the present invention.

Preparative Example 18

The procedure in Preparative Example 17 was followed, except that 1.1 parts of a 15% solution of disodium ethylene glycolate in THF were added instead of 17.3 parts of a 15% solution of sodium benzyl alcoholate in THF, to yield 7.6 parts of bis[tri(4-nitrophenyl)methoxy]ethylene (BTNPMO), an initiator [1] according to the present invention.

Preparative Example 19

In a nitrogen-replaced glass reactor, 30 parts of toluene, 5.6 parts of triphenylmethyl chloride were fed, and after stirring to a homogeneous mixture, 5.1 parts of sodium dithiolaurate was added. A white precipitation was generated. After stirring at room temperature for an hour, the white precipitation was filtered off, and the solvent and raw materials were distilled off from the filtrate under reduced pressure to yield 6.8 parts of triphenylmethyl dithiolaurate (TPMDL), an initiator [1] according to the present invention.

Preparative Example 20

The procedure in Preparative Example 19 was followed, except that 3.5 parts of sodium dithiobenzoate were added instead of 5.6 parts of sodium dithiolaurate, to yield 5.0 parts of triphenylmethyl dithiobenzoate ester (TPMDB), an initiator [1] according to the present invention.

Preparative Example 21

The procedure in Preparative Example 19 was followed, except that 3.5 parts of sodium methyloxycarbonylethyl-dithioacetate were added instead of 5.6 parts of sodium dithiolaurate, to yield 3.8 parts of triphenylmethyl methyloxycarbonylethyl-dithioacetate ester (TPMMAO), an initiator [1] according to the present invention.

Preparative Example 22

The procedure in Preparative Example 19 was followed, except that 7.5 parts of tri(4-chlorophenyl)methyl chloride were added instead of 5.6 parts of triphenylmethyl chloride, to yield 7.1 parts of tri(4-chlorophenyl)-methyl dithiolaurate (TCPMD), an initiator [1] according to the present invention.

Preparative Example 23

The procedure in Preparative Example 20 was followed, except that 8.5 parts of tri(4-nitrophenyl)methyl chloride were added instead of 5.6 parts of triphenylmethyl chloride, to yield 8.8 parts of tri(4-nitrophenyl)methyl

dithiobenzoate ester (TNPMDA), an initiator [1] according to the present invention.

Preparative Example 24

The procedure in Preparative Example 23 was followed, except that 8.1 parts of a 20% solution of bis(sodium dithiocarboxynium)ethane in THF were added instead of 3.5 parts of sodium dithiobenzoate, to yield 8.1 parts of bis[tri(4-nitrophenyl)methyldithiocarboxynium]ethane (BTNPCE), an initiator [1] according to the present invention.

Preparative Example 25

10 parts of poly(propylene glycol) (MW=1,000) was dissolved in 30 parts of toluene, and after dehydration, 0.5 parts of metal sodium were added, and reacted at room temperature for 5 hours. 11.2 parts of triphenylmethane chloride were then added, and reacted for further 5 hours to yield 18 parts of poly(propylene glycol) containing triphenylmethoxy group (PGTO), a polymerization initiator [3] according to the present invention.

Preparative Example 26

10 parts of polyester (MW=2,000), which had been obtained by reacting polyester of adipic acid and butanediol with adipic acid and which had a radical -COOH at either ends thereof, were dissolved in 30 parts of toluene. 10 parts of thionyl chloride was added, and reacted at 50°C for 8 hours. After removal of thionyl chloride at 100°C, 4.4 parts of tri(4-methylphenyl)methylcadmium chloride were added, and reacted at room temperature for 5 hours. Washing with water and removal of toluene yielded 14 parts of polyester containing tri(4-methylphenyl)methylcarbonyl group (EMTC), an initiator [3] according to the present invention.

Preparative Example 27

10 parts of hydrated polyisoprene (MW=2,500) having a radical -OH at either ends thereof, were dissolved in 30 parts of toluene. Gaseous hydrogen bromide were blown in at room temperature for one hour at the rate of 500 ml/min., while stirring. Water and then hydrogen bromide were removed under reduced pressure, and thereafter 2.9 parts of sodium tri(4-sodium sulfoniumphenyl)methylate were added, and reacted at 100°C for 2 hours. After washing with 10 parts of water, removal of toluene yielded 12.5 parts of hydrated polyisoprene containing tri(4-sodium sulfoniumphenyl)methoxy group (IPSO), an initiator [3] according to the present invention.

Preparative Example 28

After 20 parts of polyurethane (MW=5,000) of polyester (MW=1,000) of adipic acid and butanediol with tolylene diisocyanate were dissolved in 30 parts of toluene, gaseous hydrogen bromide were blown in at room temperature for one hour at the rate of 500 ml/min., while stirring. Water

and then hydrogen bromide were removed under reduced pressure, and thereafter 0.2 parts of metal magnesium were added, and reacted for 2 hours under reflux. 2.0 parts of carbon disulfide were added dropwise at 0°C, and reacted at room temperature for 5 hours. After removal of carbon disulfide, 3.1 parts of tri(4-chlorophenyl)methyl chloride were added, and reacted at room temperature for 2 hours. Removal of toluene yielded 24.7 parts of polyurethane containing tri(4-chlorophenyl)methyl-mercaptothiocarbonyl group (PUCTC), an initiator [3] according to the present invention.

Preparative Example 29

After 10 parts of ethylene-propylene random copolymer (ethylene content; 45%, MW=150,000) were dissolved with heating in 100 parts of toluene, a solution of 3.8 parts of triphenylmethoxyethyl-maleimide and 0.01 part of benzoyl peroxide dissolved in 10 parts of toluene under nitrogen seal, were added dropwise at 110°C over the period of one hour. The solution was stirred for further 3 hours under toluene reflux. Pouring the reaction solution into methanol yielded 13.5 parts of ethylene-propylene copolymer containing triphenylmethoxy group (EPTO), an initiator [3] according to the present invention.

Preparative Example 30

After 10 parts of poly(propylene glycol) (MW=1,000) were dissolved in 30 parts of toluene, gaseous hydrogen bromide were blown in at room temperature for one hour at the rate of 500 ml/min., while stirring. Water and then hydrogen bromide were removed under reduced pressure, and thereafter 2.8 parts of sodium diphenyldithiocarbamate were added, and reacted at 100°C for 2 hours. After washing with 10 parts of water, removal of toluene yielded 11 parts of poly(propylene glycol) containing diphenyldithiocarbamoyl group (PGPC), an initiator [3] according to the present invention.

Preparative Example 31

After 10 parts of ethylene-propylene random copolymer (ethylene content; 45%, MW=150,000) were dissolved with heating in 100 parts of toluene, a solution of 2.6 parts of tri(4-nitrophenyl)methoxyethyl-maleimide and 0.01 part of benzoyl peroxide dissolved in 10 parts of toluene under nitrogen seal, were added dropwise at 110°C over the period of an hour. The solution was stirred for further 3 hours under toluene reflux. Pouring the reaction solution into methanol yielded 13.3 parts of ethylene-propylene copolymer containing tri(4-nitrophenyl)methoxy group (EPNPO), an initiator [3] according to the present invention.

Preparative Example 32

The procedure in Preparative Example 31 was followed, except that 2.6 parts of tri(4-chlorophenyl)methylcarbonylpropyl-maleimide were used

instead of 2.6 parts of tri(4-nitrophenyl)methoxyethyl-maleimide, to yield 13.6 parts of ethylene-propylene copolymer containing tri(4-chlorophenyl)-methylcarbonyl group (EPCPC), an initiator [3] according to the present invention.

Preparative Example 33

The procedure in Preparative Example 31 was followed, except that 2.8 parts of dicyclohexyl-dithiocarbamoylethyl-maleimide were used instead of 2.6 parts of tri(4-nitrophenyl)methoxyethyl-maleimide, to yield 13.5 parts of ethylene-propylene copolymer containing dicyclohexyl-dithiocarbamoyl group in its side chains (EPCHTC), an initiator [3] according to the present invention.

Practical Examples 1 - 24

As shown in Tables 1 and 2, compounds prepared in Preparative Examples 1 - 24 were used in Practical Examples 1 - 24, respectively, as the radical polymerization initiator according to the present invention. As vinylic monomers, either styrene (St) or methyl methacrylate (MMA) was used. In each Practical Example, 1M of vinylic monomer and 0.5mM of initiator were added into a nitrogen-replaced glass reactor. The reactor was then degassed, and polymerization was carried out under nitrogen seal at 80°C for 6 hours. After the reaction completed, the reaction solution was poured into methanol to isolate the polymer obtained.

The yield, weight average molecular weight (Mw) and molecular weight distribution (Mw/Mn) as determined by GPC for each polymer are shown in Tables 1 and 2. The residual groups of respective initiator were verified at either ends of all polymers by NMR.

Table 1

Ex.	Vinylic Monomer	Initiator	Yield(%)	Mw(10 ⁻³)	Mw/Mn
1	St	BuTPM	18	27	1.8
2	MMA	BzTPM	19	35	1.6
3	St	MTPMO	24	35	1.5
4	MMA	BuTCPM	43	168	1.3
5	St	BzTNPM	25	29	1.8
6	MMA	BTCPME	48	370	1.8
7	St	BuTPMK	20	47	1.8
8	MMA	BzTPMK	32	65	1.8
9	St	OCTPMK	39	55	1.6
10	MMA	BTCPMK	48	422	2.0
11	St	CENPMK	38	50	2.0
12	MMA	BTNPCP	82	408	2.2
13	St	DTPME	13	20	1.8
14	MMA	BTPME	23	35	1.6
15	St	OETPME	18	25	1.5

Table 2

16	St	DTCDE	30	102	1.6
17	MMA	BTNPME	28	50	1.8
18	St	BTNPMO	52	176	1.7
19	MMA	TPMDL	24	28	1.7
20	St	TPMDB	30	67	1.8
21	MMA	TPMMA	38	30	1.4
22	St	TCPMDL	45	225	1.9
23	MMA	TMPMDA	31	50	1.8
24	St	BTNPCE	58	295	2.0

Practical Examples 25 - 37

As shown in Table 3, polymers prepared in Preparative Examples 25 - 34 and having functional groups for radical polymerization, and polymers obtained in Practical Examples 6, 12, 18 and 24 (abbreviated as NPM-MMA, PCP-MMA, PMO-St and PCE-St, respectively) were used. As vinylic monomers, either styrene (St) or methyl methacrylate (MMA) was used. In each Practical Example, 1M of vinylic monomer, and polymers having functional groups for radical polymerization in the amount corresponding to 0.5 meq. of said functional groups were added into a nitrogen-replaced glass reactor. The reactor was then degassed, and polymerization was carried out under nitrogen seal at 80°C for 6 hours. After the reaction completed, the reaction solution was poured into methanol to isolate the polymer obtained.

The weight average molecular weight (Mw) and molecular weight distribution (Mw/Mn) as determined by GPC, as well as % contents of block and/or graft matters (block rate) as determined by solvent fractionation, for each block and/or graft copolymers (A-B-A-type block matter in Practical Examples 25 - 26, 28, 30 and 34 - 37, block/graft matter in Practical Example 27, and graft matter in Practical Example 29, and 31 - 33) are shown in Table 3.

Table 3

Ex.	Monomer	Initiator	Mw(10 ⁻³)	Mw/Mn	Block Rate
25	St	PGTO	2.5	1.9	95
26	MMA	EMTC	3.0	3.9	85
27	St	IPSO	4.3	2.2	89
28	MMA	PUCTC	11	4.5	87
29	St	EPTO	230	8.9	87
30	St	PGPC	1.9	1.9	93
31	MMA	EPNPO	220	8.5	79
32	St	EPCPC	240	7.8	80
33	MMA	EPCHTC	285	7.6	88
34	St	PME-MMA	555	2.3	74

35	St	PCP-MMA	603	2.5	78
36	MMA	PMO-St	275	2.3	79
37	MMA	PCE-St	425	2.2	80

[Effects of the Invention]

The radical polymerization initiator [1] and macromolecular radical polymerization initiator [8] according to the present invention are capable of initiating living radical polymerization. The process [2] according to the present invention, which involves the use of the initiator [1], has several advantages over the processes using prior art initiators for living radical polymerization, including phenylazotriphenylmethane; i.e., the process enables: (1) to obtain polymers with narrower molecular weight distributions, even when increased molecular weights are to be attained; (2) to obtain polymers having various functional groups introduced at either ends thereof; and (3) to synthesize star polymers.

The process [4] according to the present invention, which involves the use of the initiator [3], enables: (4) to obtain block and/or graft polymers with elevated yields; and even (5) to obtain block and/or graft polymers between incompatible segments. Using initiators based on non-vinyl polymers in particular among the initiators [3], said process [4] enables (6) to obtain with elevated yields block and/or graft polymers of non-vinyl polymers and vinyl polymers, which have not been available with prior art polymerization initiators.

Due to the above-mentioned effects exerted by the present invention, the polymer compositions obtainable by the present processes using the radical polymerization initiators according to the present invention are particularly useful, are applicable to a wide variety of molded materials and additives thereto, macromolecular activators, binders, adhesives, thickeners, viscosity-index enhancers, flocculants, water absorbents, compatibility enhancers, dispersants and others, and can be used in various raw materials for synthetic resins, compatibility enhancers and others, as polymers having terminal functional groups.